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14. ABSTRACT

We studied the assembly of a system composed of diketopyrrolopyrrole (DPP) donors with chiral and achiral side chains that can form triple Hydrogen-bonds with perylene diimide (PDI) acceptors to form hierarchical superstructures. The homoaggregation of the individual components as well as heteroaggregate formation, as a result of ?•••? stacking and H-bonding, were studied by variable temperature UV/Vis and CD spectroscopies and electronic structure theory calculations. It was found that, upon cooling, the achiral PDIs bind to disordered DPP stacks, which drives the formation of chiral superstructures. A new thermodynamic model was developed to

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Inducing the formation of functional macroscopic assemblies through programmed orthogonal supramolecular interactions: Final report.

ABSTRACT

We studied the assembly of a system composed of diketopyrrolopyrrole (DPP) donors with chiral and achiral side chains that can form triple Hydrogen-bonds with perylene diimide (PDI) acceptors to form hierarchical superstructures. The homoaggregation of the individual components as well as heteroaggregate formation, as a result of ?•••? stacking and H-bonding, were studied by variable temperature UV/Vis and CD spectroscopies and electronic structure theory calculations. It was found that, upon cooling, the achiral PDIs bind to disordered DPP stacks, which drives the formation of chiral superstructures. A new thermodynamic model was developed to describe quantitatively this novel assembly process.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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Received	Paper
11/19/2013 3.00	Stephen Rieth, Zhong Li, Charlotte E. Hinkle, Carmen X. Guzman, Jungeun J. Lee, Samer I. Nehme, Adam B. Braunschweig. Superstructures of Diketopyrrolopyrrole Donors and Perylenediimide Acceptors Formed by Hydrogen-Bonding and ?···? Stacking, The Journal of Physical Chemistry C, (05 2013): 0. doi: 10.1021/jp400918z
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(1) 2012 Gordon Research Conference, Donor-Acceptor Systems, Salvia Regina, Rhode Island "Donor-Acceptor Crystalline Supramolecular Polymers"

(2)2012 Gordon Research Conference, Electronic Processes in Organic Materials, Il Ciocco, Italy "Photoactive Donor-Acceptor Crystalline Supramolecular Polymers"

(3) 244th American Chemical Society National Meeting, Philadelphia, PA, World Class University International Symposium on Energy Storage and Conversion, "Donor-Acceptor Crystalline Supramolecular Polymers for Solar Energy Harvesting"

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TOTAL:

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Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Charlotte Hinkle	0.50
Zhong Li	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Adam B. Braunschweig	0.03	
FTE Equivalent:	**0.03**	
Total Number:	**1**	

Names of Under Graduate students supported

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Total Number:	

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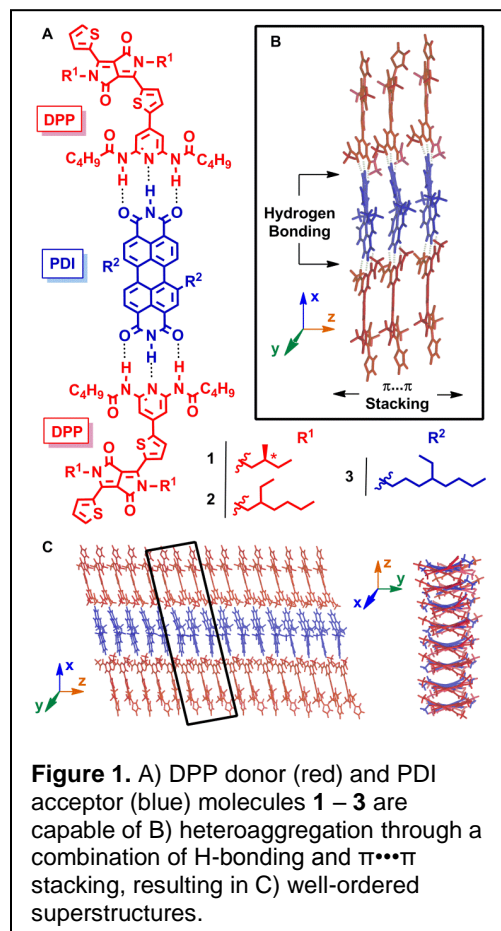
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FINAL REPORT W911NF1210125. Inducing the Formation of Functional Macroscopic Assemblies Through Programmed Orthogonal Supramolecular Interactions. PI. Adam B. Braunschweig, University of Miami, Coral Gables, FL 33146. Email: a.braunschweig@miami.edu.

Figure 1. A) DPP donor (red) and PDI acceptor (blue) molecules **1** – **3** are capable of B) heteroaggregation through a combination of H-bonding and π•••π stacking, resulting in C) well-ordered superstructures.

1. Statement of the Problem Studied. The goal of the proposed work was to develop self-assembling materials that form complex architectures and emergent stimuli-responses as a result of complementary supramolecular interactions. While this approach to achieving functional molecular architectures is common in natural materials, researchers have been unable to prepare systems with emergent properties and sophisticated stimuli responses comparable to biological materials. The innovation of the proposed research derives from this simple idea: that materials where the position of each atom in the structure is defined precisely can be obtained by programming primitive interactions onto complementary small molecule scaffolds and thereby overcome the disorder that is characteristic of most organic and polymeric materials. This approach represents a straightforward route towards addressing the enormous challenge of supramolecular engineering and is a first step towards achieving biomimetic sophistication with synthetic systems.

2. Summary of Most Important Results.

The most important result obtained was the synthesis of molecular components that assemble into complex architectures, and the study of the interaction between these complementary components to develop a new quantitative model for their aggregation into heterosuperstructures. The aggregation of chiral and achiral diketopyrrolopyrrole-based (DPP) donors with a 1,7-substituted perylene diimide (PDI) acceptor (Figure 1A) was studied by various spectroscopyic methods. Upon mixing in solution, the PDI and DPPs assemble into well-ordered superstructures (Figure 1C) because of: (1) complementary triple H-bonds along one spatial axis (x), (2) large aromatic surfaces that drive aggregation via π•••π stacking along an orthogonal axis (z), and (3) solubilizing alkyl chains appended to each aromatic core that can interact along the third orthogonal axis (y) (Figure 1B). Chiral side chains have been introduced onto the DPP donor **1** so distinct Cotton effects that arise as a result of the formation of chiral superstructures can provide additional information on the emergence of order.[1] Variable temperature (VT) UV/Vis and CD spectroscopic measurements revealed that the PDIs associate to disordered DPP aggregates, which subsequently reorganize into helical heteroaggregates of a single chirality. A new thermodynamic model was developed that quantifies the binding parameters ($\Delta H°$ and $\Delta S°$) associated with each interaction (H-bonding and π•••π stacking) and, with the aid of electronic structure theory calculations, elucidates the subtle supramolecular cues that induce the transition from disordered aggregates into well-defined helices.

DPP donors **1** and **2** have diamidopyridine (DAP) groups, which can form triple H-bonds with the diimide groups of PDI acceptor **3** (Figure 1a). The donors differ only by their *N*-alkyl chains: **1** possesses homochiral (S)-2-methylbutyl side chains, and **2** has racemic 2-ethyloctyl chains. Like complex biological systems, these assemblies form from the combined effects of multiple noncovalent interactions working in unison, and the aim of this study was to derive models that describe how the effects of each individual interaction contribute to the formation of the resulting superstructure. Initially, the homoaggregation of **1** and **3** were analyzed independently by UV/Vis spectroscopy to understand the role homoaggregation plays in the formation and structure of heteroaggregates. This is an important initial study because the aggregation of heteroaggregates is so complex that the aggregation of the individual components must first be investigated and understood, so their contribution to the heteroaggregates can be accounted for. The UV/Vis spectrum of **1** in toluene displays absorption maxima at 538 and 580 nm at 25°C, which are the result of dipole allowed S_0–S_1 electronic transitions. These bands undergo bathochromic shifts with increasing sharpness, which are spectral signatures of J-type aggregation (Figure 2A). Although π-stacked chromophores with chiral side-chains often form chiral superstructures,[1] the absorbance intensities of **1** exhibit a sigmoidal dependence with temperature and no signal was observed in VT CD experiments.[2] These observations are characteristic of isodesmic stacking, where the K_as describing the π•••π stacking is constant regardless of aggregate size.[3] By fitting the changes in absorbance of **1** with changes in temperature to an isodesmic model,[4] an excellent fit was obtained to provide $\Delta H°$ and $\Delta S°$ values of –7.4 ± 0.5 kcal mol^{-1} and –3.0 ± 2.0 e.u. respectively, indicating the π•••π stacking is enthalpically driven (Figure 2B). DFT calculations (B3LYP/6-31G(d,p)) on homoaggregates of a DPP that has methyl side chains to simplify the calculation revealed a slip-stacked binding geometry with thiophenes overlapping the DPP cores (Figure 2C and 2D). This calculated structure is consistent with the UV/Vis data and a similar slip-stacked geometry observed previously in an X-ray crystal structure of DPP-thiophene oligomers.[5] The energy of binding, ΔE = –10.5 kcal mol^{-1}, from the DFT calculations agrees well with the $\Delta H°$ derived from the fitting.

Figure 2. A) VT UV/Vis spectra of a 20 µM solution of **1** in toluene. B) The absorption peak at 540 nm in the VT UV/Vis of **1** fit to an isodesmic model. C) Top and side view of a DFT structure of a π•••π stacked DPP dimer. D) VT UV/Vis spectra of a 35 µM solution of **3** in toluene. E) The absorption peak at 592 nm in the VT UV/Vis of **3**. F) Top and side view of a DFT structure of a π•••π stacked PDI dimer. Dashed lines are run along the *N–N′* axis, and are shown to indicate the twist angle between the stacked PDIs.

The aim of this project was to incorporate several different types of noncovalent interactions into the superstructures to obtain unprecedented control over hierarchical assembly in organic materials, and to control aggregation, each of the individual interaction must be investigated qualitatively and quantitatively. H-bonding is known to affect the supramolecular assembly of 1,7-substituted PDIs, so the homoaggregation of **3** was also investigated by VT UV/Vis spectroscopy. The UV/Vis spectra of 1,7-
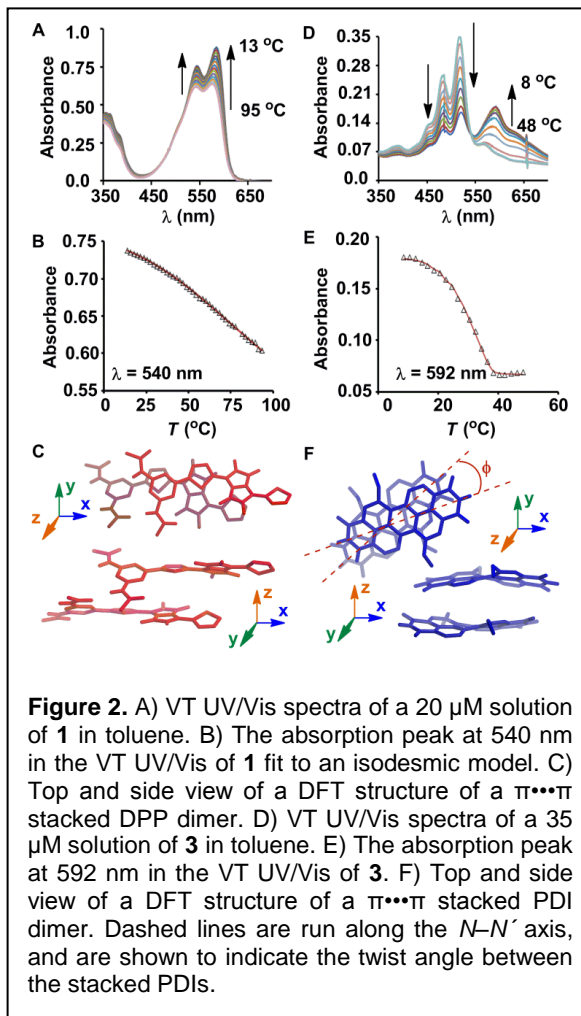
substituted PDIs typically display characteristic peaks arising from the $S_0 - S_1$ transition[6] that are broadened because of twisting in the perylene ring system[7] that inhibits aggregation beyond π-stacked dimers.[8] Previously studied PDIs without N-substituents display a sharp peak that are assigned to the J-aggregation of π•••π stacked dimers interconnected by H-bonding.[9] For PDI **3**, the UV/Vis spectra revealed a sharp absorbance maximum at 520 nm in toluene with a pronounced vibronic fine structure. Upon cooling, these peaks decrease with a concomitant increase of a broad band with a maximum at 592 nm (Figure 2E). These spectral changes are similar to non-1,7-substituted PDIs whose π•••π aggregation is intermediate between J- or H-type[10] as a result of rotationally-displaced stacked PDIs.[11] DFT calculations of a π•••π stacked dimer of **3** revealed an offset, φ, of 22° between the long axes (Figure 2F) and thus, we deduce that the new absorption peak to a similar stacking geometry. A plot of the absorbance at 592 nm versus temperature reveals negligible aggregation above 37 °C. Below 37 °C, the absorption increases quickly, suggesting nucleation-growth assembly[12] —where an initial disfavored binding event precludes association until a critical temperature is reached, after which a new thermodynamically favored equilibrium drives the assembly into π-stacked superstructures (Figure 2F). Suspecting intermolecular H-bonding plays a key role in assembly, the VT UV/Vis experiment was repeated with a bis-*N*-cyclohexyl derivative of **3** or in 3% DMSO in toluene, both of which inhibit H-bonding.[2] No spectral changes that indicate π-stacking were observed in either control experiment, confirming that H-bonding promotes the π-stacking of **3**. These investigations into the homoaggregation of **1** and **3** are necessary to understand how the self-assembly of the individual components contributes to the structure and assembly of the multicomponent heteroaggregate assemblies.

Heteroaggregation arising from H-bonding and π•••π stacking was investigated by VT UV/Vis spectroscopy on a 2:1 mixture of **1** and **3**, respectively, in toluene. At 40 °C, the spectrum is a linear composite of the individual spectra (Figure 3A), indicating that mixed π-heteroaggregates are not present at high temperature. Upon cooling, the absorbance maxima of **3** decrease and two new bands arise at 563 and 615 nm, which are assigned to a S_0–S_1 transition from the π•••π stacking of **3**. Several aspects of the spectrum indicate heteroaggregate formation: 1) the absorbance at 615 nm begins to increase in the mixture at 21 °C, which is a much lower temperature than was observed for the onset of homoaggregation of 3 (39 °C), 2) the new bands at 563 and 615 nm are much sharper than the broad peaks formed by homoaggregates of **3**, suggesting J-type aggregation, meaning the π-stacked PDIs adopt a different geometry in the heteroaggregates, and 3) the change in the absorption at 615 nm for the mixture of **1** and **3** is more

Figure 3. A) VT UV/Vis and B) CD spectra of a 70 µM solution of **1** in toluene with 0.5 molar equivalents of **3**. C) The absorbance (◇) and elipticity (Θ) at 615 nm obtained by VT UV/Vis and CD respectively fit to a cooperative helix formation model.[11] D) Top and side view of the DFT structure of the H-bonded and π•••π′ stacked **1:3** dimer. Dashed lines are run along the *N–N´* axis, and are shown to indicate the twist angle between the stacked PDIs.

gradual (Figure 3C) than for the homoaggregates of **3**, suggesting that homoaggregation pathways are suppressed and a different assembly mechanism is operating that is driven by the triple H-bonding between **1** and **3**. Prior to the appearance of the PDI π-stacking bands 563 and 615 nm, the transitions
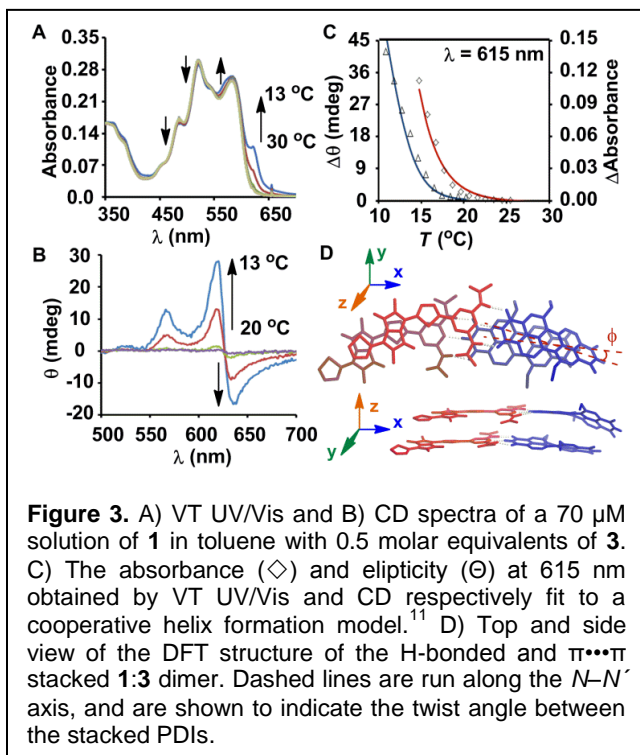
previously assigned to π-stacking of 1 (538 and 580 nm) increase steadily with decreasing temperature, suggesting extensive homoaggregation of **1** precedes heteroaggregate formation. A bisignated Cotton effect, with peaks at 563 and 615 nm, matching the π-stacking peaks of the achiral PDI, appeared in the VT CD spectra. The bisignated effect is a consequence of electronic coupling between conjugated segments in a helical array (Figure 3B).[13] Notably, the transition temperature in the VT CD spectrum of the heteroaggregates is 5 °C lower than in the UV/Vis measurements, suggesting that only after the association of several molecules of **3** onto disordered aggregates of **1** does the rearrangement into chiral heteroaggregate helices occur (Figure 3C), and the emergent chirality in these superstructures is the direct result of the PDI solubilizing chains interacting along the y-axis. The VT UV/Vis experiments were repeated in a mixture of **2** and **3** (Figure S5), and while the same trends were observed in the VT UV/Vis spectra, no Cotton effect arose in the CD spectrum of **2** and **3**.[2] The structure of the heteroaggregate of **1** and **3** was modeled by DFT calculations using methyl and ethyl solubilizing chains on DPP and PDI, respectively. While the relative orientations of the DPPs in the heteroaggregates remain relatively unchanged compared to the homoaggregates, the π-offset, φ, between PDIs in the heteroaggregates (11°, Figure 3d) changed significantly compared to PDI homoaggregates (22°), indicating that the preferred conformation of the DPPs dictates the π•••π stacking angle in the heteroaggregate superstructure. The assessment of PDI J-aggregation from the VT UV/Vis spectrum of the heteroaggregate is supported by the head-to-tail arrangement of the PDIs in the calculated structure (Figure 3D).[14] These observations suggest that a new assembly mechanism that has not been described previously in supramolecular systems is directing the formation of these hierarchical donor-acceptor structures.

The spectroscopic data were used to derive a new quantitative assembly model that describes formation of heteroaggregates that arise from both H-bonding and π•••π stacking. The corresponding thermodynamic parameters for each interaction were obtained by fitting the changes in absorption with temperature to this model. There exist few quantitative models that describe the formation of heteroaggregates that employ multiple orthogonal interactions.[4] The data indicate that PDIs bind to disordered stacks of DPPs to produce chiral superstructures

Figure 4. The proposed model for the heteroaggregation of the DPPs (red tiles) and PDIs (blue tiles) into chiral assemblies.

(Figure 4), which leaves an available H-bonding site on each PDI that can potentially be occupied by an additional DPP at higher concentrations. In the model (Figure 4), disordered homoaggregates of **1** assemble isodesmically according to the microscopic binding constant K_1. Since there are four identical pathways by which this process can occur, K_1 is one-fourth the experimentally observed macroscopic K_a. The initial association event of one molecule of **3** to a stack of **1** of any size is governed by microscopic association constant K_2 (Figure 4B). As there are two positions where H-bonding takes place in **3** and n points on a stack of **1**, where n denotes the number of residues, the macroscopic K_a is $2nK_2$. Further association of 3 to the stacks are described by K_2 and K_3, where K_3 is a dimensionless K_a that includes the energy contributions from π•••π stacking and any chelate cooperativity effects[15] (Figure 4) associated with the aggregation of **3** within the **1** stacks. The resulting mass balance equations can be written as infinite series that describe the total concentration of each species, $[PDI]_t$ and $[DPP]_t$, as a function of n that are both convergent and can be solved to obtain [PDI] and [DPP] for any value of K_1, K_2, K_3, $[PDI]_t$, and
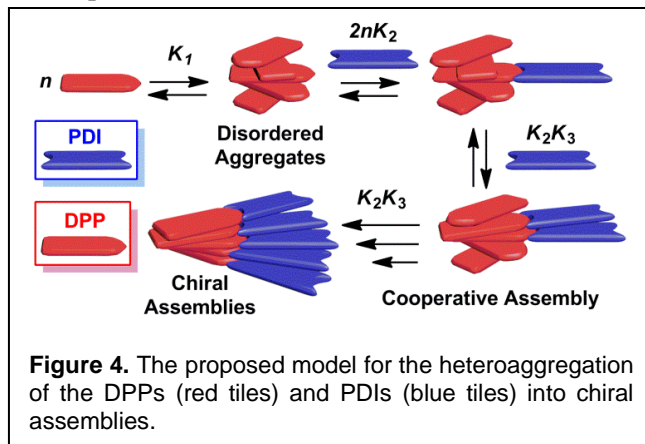
[DPP]$_t$. $\Delta H°$ and $\Delta S°$ corresponding to K_1 were fixed to the values previously obtained by studying the homoaggregation of **1** and held invariant. This new model can be used to make predictions about the assembly of hierarchical systems that form as a result of multiple orthogonal interactions, in particular when some of these interactions only arise in the heteroaggregate – a hallmark of complexity in biological assembly – and thus cannot be measured by studying the individual components. When both VT UV/Vis and CD measurements were simultaneously fit to the same parameter set, the $\Delta H°$ and $\Delta S°$ for K_2 (–24.1 ± 0.1 kcal mol^{-1} and –70 ± 2 e.u.) and K_3 (–13.5 ± 0.1 kcal mol^{-1} and –40 ± 1 e.u.) were obtained. These numbers compare well to the values of ΔE of –17.8 kcal mol^{-1} and –6.3 kcal mol^{-1}, respectively, found by electronic structure theory calculations, although the calculations may underestimate the enthalpy by not accounting fully for cooperative stabilization. These thermodynamic parameters indicate that K_2 is enthalpically driven, which is typical for H-bonded dimers. Interestingly, K_3 is also enthalpically driven, but an entropic penalty is associated with the rearrangement of **3** into J-aggregates, presumably because the contorted perylene rings disfavor this stacking geometry. Nevertheless, the enthalpy associated with π-aggregation overcomes the disfavorable entropy below room temperature, which drives heterosuperstructure formation upon cooling.

The self-assembly of heteroaggregates comprised of π-conjugated donors and acceptors could lead to synthetic hierarchical structures with functional complexity comparable to their biological counterparts, but models are needed that can describe the complex milieu of interactions involved in superstructure formation. By studying the heteroaggregation of a DPP donor and PDI acceptor, a new model was developed that elucidates the subtle structural cues that induce the transition from a disordered aggregate into a chiral helix. Using this new model, all thermodynamic parameters were quantitatively determined, and both H-bonding and the subsequent helix formation process were found to be enthalpically favored but entropically disfavored. This new model could be used to create ordered superstructures of donors and acceptors, which are increasingly investigated in the context of photovoltaics and for understanding fundamental aspects of charge and energy transport in self-assembled systems. It should be noted that, like the system described herein, natural self-assembled systems utilize multiple orthogonal noncovalent interactions that work in unison to form functional hierarchical nanostructures, thereby achieving "complexity out of simplicity", which remains an elusive goal for chemists.[16]

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